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THE STEARATES IN THE PROTECTIVE COATINGS INDUSTRY

By FRANCIS J. LICATA, Chief Chemist, Metasap Chemical Company, Inc., Harrison, N. J.

The protective coatings industry has many uses for stearates. These include thickening, suspension, and flatting in paints, varnishes, enamels, lacquers, sealers, stains, silk screen extender base, cement water paints, waterproofings, paint removers, and other applications. A description which is to follow of the basic properties of the stearates shows why they are necessary in the products just mentioned and, in addition, may suggest to you other uses in your various formulations.

In starting, I might say that the stearates to be described are manufactured by precipitating a solution of sodium stearate with a water solution of the desired metal. The resulting precipitate is then filtered, washed and dried at a low temperature to preserve the very fine particle size. The dried filter cake is disintegrated and blown by air into cyclone separators from which it is filled into standard 50-pound cartons.

The stearates are useful because they are fine powders having the properties of both organic and inorganic matter. They have rather high melting points and may be considered as soft pigments. Too, they are highly water repellent and some of them will dissolve in organic liquids to form gels. The stearates lend themselves to a variation in composition so that each stearate can be made into a family of slightly different products having a range of properties and uses. For instance, there may be five or six different modifications of aluminum or zinc stearate, each serving a specific purpose.

Paper presented at the thirteenth annual convention of the Southern Paint and Varnish Production Club, in Biloxi, Miss., March 9-11, 1949. This paper will be published in a later issue of the Official Digest.

General Properties

The products I am going to describe are all fine, white bulky powders. They have a characteristic fatty odor. Like pigments in general they are composed of clusters of individual particles whose ultimate size is one micron or less in diameter. When examined by the microscope, they appear colorless and tranparent. Their refractive index ranges between 1.360 and 1.61. Although they are a little heavier than water with specific gravities ranging between 1.009 and 1.323, they are so water repellent that they float even in boiling water. Some of them have a greasy or unctuous texture, while others feel dry and will not stick together when compressed. The melting points reveal several interesting features of the stearates. Some of them, like zinc stearate, fuse to a thin liquid within a narrow temperature range. Others, like aluminum stearate, show an initial softening point and become viscous liquids up to a much higher temperature. Some will not fuse at all but will char and decompose.

Chemically these substances are quite similar in that they are decomposed by mineral acids and alkalies. In general they are saturated and rather inert compounds, insoluble in all kinds of liquids. The only exception is aluminum stearate. It will dissolve to form gels in a number of substances, such as hydrocarbons and large molecular weight esters whose properties resemble the hydrocarbons. Table I presents in a condensed form some of the more important properties of the most commonly used stearates.

TABLE I—General Properties of Searates

Property	Aluminum	Calcium	Lead	Magnesium	Zinc
Specific Gravity	1.010	1.041	1.323	1.028	1.056
Refractive Index	1.36–1.39	1.40–1.50	1.50–1.55	1.50–1.55	1.50–1.55
Softening Point	145°C.	150°C.	100°C.	150°C.	118°C.
% Oxide	8.0	10.0	28.0 (Pb.)	8.0	15.5
% Free Stearic Acid	12.0	nil	nil	nil	nil
Solubility	G	PS	PS	PS	I
% Retained on					
100 mesh	0.0	0.0	0.0	0.0	0.0
200 mesh	2.0	0.0	0.0	0.0	0.0
325 mesh	5.0	0.1	0.1	0.0	0.0
400 mesh	..	0.2	..	0.0	0.1

I—Insoluble.

PS—Partly soluble and may form pastes in hydrocarbons, chlorinated solvents, turpentine, and so forth.

G—Will form gels in hydrocarbons, chlorinated solvents, turpentine, oils, waxes and resins.

Application of the Various Stearates

The value of a substance depends on the possession of desirable characteristics not possessed by other substances and also on its ability to combine with something else to produce an entirely new product having particular properties. The stearates have both of these traits. They are useful because of their own intrinsic value and because in combination with other substances they produce new and desirable materials. Let us consider some of the stearates individually.

Calcium Stearate

This is a white powder having a small particle size. It passes completely through a 325 mesh screen and most of the particles are finer than that. Because of this fineness calcium stearate has a great covering power and is used in cement water paints for waterproofing. As little as a fraction of one per cent is incorporated in various hygroscopic substances to prevent caking in storage. It is also used in a large number of powdered waterproofing compounds for concrete and stucco. Its softening point is about 150° C. and it is difficult to find anything into which it will remain dissolved. If heated high enough, calcium stearate will dissolve in various solvents; however, on cooling there is a tendency to come out of the solution and form soft, smooth, cloudy pastes which may be thixotropic. Because of its limited solubility, calcium stearate is used in semi-gloss enamels, to a limited extent in flatting varnishes and lacquers, and to reduce the thickening effect of aluminum stearate in extender base for silk screen printing. Calcium stearate is a very stable and unreactive powder, hence is only little used in the protective coatings industry.

Lead Stearate

Very little will be said about this stearate because it is little used in this industry outside of stabilizing polyvinyl polymers. It is of no value as a drier because of its poor solubility. In general its properties are very similar to other less expensive stearates.

Magnesium Stearate

This product is also a fine, white powder which is highly water repellent and shows little tendency to dissolve. Its most outstanding property is its extremely fine particle size. It goes completely through a 400 mesh screen but in reality is much finer. It is the finest and fluffiest stearate known, it has a fatty or greasy texture; it is very adhesive and has a tremendous covering power. As a result it is used chiefly in cosmetics and pharmaceutical tablet manufacture. In addition, it has limited application as a flatting agent and in the general thinning of aluminum stearate gels because its solvency is somewhat between aluminum stearate and the other divalent stearates.

Zinc Stearate

This stearate probably is most generally known to the layman because of its household use in face and body powders. For practical purposes it is odorless and colorless. Its refractive index is 1.50 to 1.55 and it has a relatively low and sharp melting point. The most outstanding characteristic of zinc stearate is its extremely small particle size, which is exceeded possibly only by magnesium stearate. This product also passes completely through a 400 mesh screen but it is much finer than this screen test is able to indicate. The microscope shows that the particles may be less than one micron in diameter. As a result of the extremely small particle size this stearate has a tremendous specific surface. A rough estimation of the film area is about 25,000 sq. cm. per gram. Therefore, most of the uses of zinc stearate are based on the fact that a little will cover a large surface. On the other hand, it is one of the most insoluble stearates. On heating with solvents, it will melt and seem to dissolve, but on cooling this stearate will come out of solution in particles larger than the original powder used.

It is safe to say that zinc stearate is used when an extremely fine, bulky, soft, water repelling, colorless and inert pigment is required. Consequently, fairly large quantities are employed in cement water paints and rock wool insulation, because only a small percentage will cover a large number of particles or fibers with a water repell-

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ing surface. Small quantities in paints having a high zinc oxide content are used to increase their durability. The fact that zinc stearate does not form gels even at high temperatures allows it to be used in semi-gloss enamels and to a limited extent for flatting varnishes and lacquers. The largest use of zinc stearate in this industry is for sanding sealers.

Sanding Sealers

In this case, advantage is taken of the fact that zinc stearate has a desirable refractive index, to fill the pores of wood, is colorless and softens nitrocellulose films just enough to allow good sanding. Ordinarily zinc stearate is ground for about 24 hours as a 25 per cent concentrate in a lacquer having about 20 per cent total solids. A ground concentrate should flow easily out of the pebble mill and should blend into clear lacquer. Usually the zinc stearate is well dispersed as a very large number of extremely fine inert particles throughout the lacquer film. However, its extreme fineness is both a blessing and a source of trouble because its specific surface becomes greater as the particle size is decreased and surface activity becomes evident more and more.

Let us digress for a moment to consider how the surface increases as a particle is broken down. A cube with sides of 1 cm. has a volume of 1 cc. and a surface of 6 sq. cm. If this is broken into smaller cubes, each with a side of 1 mm. or one-tenth of the orginal, there will be 1,000 cubes with a total surface of 60 sq. cm., although the total volume remains the same. An inspection of Table II shows that when the cubes have been

TABLE II—Specific Surface

Length of Side	*No. of Cubes*	*Total Surface*
1.0 cm.	1	6 sq. cm.
1.0 mm.	1,000	60 sq. cm.
0.1 mm.	1,000,000	600 sq. cm.
0.01 mm.	1,000,000,000	6,000 sq. cm.
0.001 mm.*	1,000,000,000,000	60,000 sq. cm.

*(1 micron)

reduced so that each side is, roughly, one-thousandth of a millimeter or one micron, there will be one trillion particles with a total surface of 60,000 sq. cm. It is also interesting to note that when particles reach this reduced size, they begin to show Brownian movement when dispersed. Is it any wonder that sometimes zinc stearate causes excessive thickening on grinding in a pebble mill?

Although zinc stearate is one of the most insoluble stearates, there will be excessive thickening if the grinding is too efficient, if the zinc stearate is too fine, or if the stearate is slightly more soluble than it should be, because each of these factors will tend to produce such a fine degree of dispersion that surface activity and colloidal phenomenon are unavoidable.

As mentioned above, stearate particles are really clusters of small individual particles like a bunch of grapes. Grinding serves to break these clusters into smaller clusters with fewer grapes in each bunch. It is readily evident that continued grinding will ultimately reduce the clusters to numerous individual particles having very small dimensions and great surface activity. The thickening of milled concentrates may be compared to the formation of foams or creams where surface activity combines liquids and gases to form rigid structures.

To avoid this excessive thickening it is necessary to reduce the time of grinding or use a coarser stearate. If a batch has already been thickened too much, the use of two or three per cent of 2-amino-2-methyl-1-propanol will thin it out sufficiently without any injurious effects.

Aluminum Stearate

This product is the most useful of this group because it possesses all the characteristics of the other stearates, and in addition, combines with a large number of substances to form gels. As a matter of fact aluminum stearate is the backbone of the stearate industry. Like other stearates, it is an odorless, bulky, and colorless powder. It is not as fine or bulky as calcium or zinc stearates but is as soft and water repelling. The refractive index is such that when ground in varnishes and lacquers it results in transparent films. The melting point covers a wide range. Chemically it is different from other stearates in that it is never a pure chemical compound but always contains some free fatty acid. In addition it combines with a large number of solvents, oils, waxes, and resins to form gels which have many valuable technical applications. This phenomenon of gelling is so important that it is worth receiving extended consideration.

Each type of solvent produces a different degree of dispersion of aluminum stearate and therefore results in gels having different structures, such as slightly viscous liquids, rigid, buttery gels or thixotropic pastes. None of the stearates are soluble in water or polar compounds. In fact if these are added to aluminum stearate gels, they will cause thinning and finally throw the stearate out of solution. The following is a brief description of what aluminum stearate will do with various solvents.

Aromatic solvents like toluol and benzol are the best solvents for aluminum stearate; they require only 110° F. to form gels which are permanently elastic and transparent. These gels slow down the rate of solvent evaporation and dry to transparent and glossy films.

Aliphatic hydrocarbons, like mineral spirits, are poorer solvents and require a higher temperature of about 180° F. to form elastic and transparent gels. However, this type of solvent produces metastable gels. On aging they become cloudy, buttery pastes which are easy to grind and mix with other ingredients. Poorer solvents of this kind may develop syneresis. As the molecu-

lar weight becomes higher, the solvency for aluminum stearate becomes better and the resulting gels are rigid and buttery but remain permanently transparent. Hence, the boiling point of the mineral thinner offers a control over the type of gel to be obtained.

Waxes and resins which are soluble in hydrocarbons also act as solvents for aluminum stearate and form hot, viscous gels with a higher melting point range. On cooling, these mixtures remain compatible with each other so that when dissolved serve to increase the viscosity of the solution and at the same time keep the resin in solution.

All sorts of animal, marine and vegetable, except castor, oils, dissolve aluminum stearate at about 350° F. They form permanent transparent and viscous solutions. The anomalous behavior of castor oil is explained by the fact that it contains a hydroxyl side group and is somewhat polar.

In general, low molecular weight polar compounds having a high dielectric constant do not dissolve aluminum stearate but, as their molecular weight increases by a lengthening of the carbon chain, the polarity and dielectric constant decrease while the solvency for aluminum stearate increases. This offers another means of controlling the type of gel.

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Before leaving this subject the general gelling phenomenon will be described. Nothing happens on thoroughly mixing solvent and aluminum stearate while cold or while increasing the temperature up to a certain critical temperature depending on the solvent. This is the gelling point. When this point is reached, there is a sudden increase of viscosity and a general clarification. As the temperature is increased further, there is a decrease in viscosity, indicating a finer degree of dispersion and a greater degree of thermal agitation of the stearate molecule. On cooling to room temperature the resulting gels are different depending on the rate of cooling and solvency of the vehicle.

Thus far aluminum stearate has been described as an individual substance having a great deal of usefulness because of its gel forming properties. Aluminum stearate is even more interesting; it can be modified to produce a whole group of stearates having slightly different properties each useful for a specific purpose. Aluminum stearate can be modified so that the melting point, metal content, free fatty acid, and gelling property are increased or decreased. Table III illustrates a few popular grades of aluminum stearate.

TABLE III—Various Aluminum Stearates

Grade	*Softening Point*	*Washed Ash*	*Free Fatty Acid*	*Gelling Power*
Aluminum Stearate—				
V	100°C.	6.0%	30%	(1)
XX	120°C.	7.0%	20%	(2)
R	145°C.	8.0%	12%	(3)
GM	150°C.	9.0%	6%	(4)
Metasap 537	160°C.	10.0%	5%	(5)

(1) Least; (2) Little; (3) Medium; (4) High; (5) Most.

Please note the inverse relationship between the washed ash and the free fatty acid. The stearate which contains the least ash has the highest free fatty acid and the least gelling power. On the other hand, the stearate having the highest washed ash has the least free fatty acid and has the highest bodying power.

It is obvious that a substance which shows such a wide variation of behavior will lend itself to many technical applications. The following are a few of the most important ones.

Stains

Because of its thickening power aluminum stearate is used in stains to minimize the penetration so that a heavier color deposit is obtained on the surface rather than to have it migrate into the wood or other porous surfaces.

Paint

Aluminum stearate is almost universally used in flat wall paints to prevent hard settling of pigment. This is accomplished in two ways; namely, by actually hindering the settling of pigment because of the thickening effect of the stearate and by forming a layer around each pigment particle. When the pigment particles finally do settle, this stearate layer prevents their cohesion. As a result a mild agitation will be sufficient to redisperse the pigment throughout the vehicle.

Aluminum stearate may be introduced into paint in several ways. One method is to mix as a dry powder with the other pigments and then grind into the vehicle. About 2 per cent stearate based on the weight of the pigments is used and the frictional heat developed during grinding causes the stearate to dissolve in the vehicle. A better method is to form a gel beforehand and then grind the gel with the other ingredients. This method is preferable because there is definite assurance that all the stearate is dissolved and as a consequence less of it may be necessary. Gels may be produced by heating 5 per cent to 10 per cent of aluminum stearate in linseed oil to about 350° F. Another method is to substitute mineral spirits for linseed oil in which case a temperature of 180° F. will be sufficient. The use of a small percentage of methanol, butanol or various metallic soaps will have a thinning effect and at the same time tend to stabilize the mineral spirits gel.

Aluminum stearate gives a puffing and an antisagging effect to paint.

Flatting

Aluminum stearate is the best flatting agent. For this purpose it should not be allowed to gel but should be dispersed as an inert pigment. Aluminum stearate has a refractive index which allows it to be used in varnishes or lacquers as a transparent flatting agent in order to reveal the full beauty of the grain of the wood. Because it is a soft pigment aluminum stearate imparts a smooth and velvety texture to flat finishes. However, the most desirable characteristic is that aluminum stearate will not settle nor cake. This makes it superior to other flatting agents. Ordinarily aluminum stearate is ground at a 20% to 25% concentration in a high volatile content varnish or lacquer in a pebble mill until a uniform dispersion is obtained. This concentrate is then added to clear varnish or lacquer until the desired degree of flatting is obtained.

Flatting is mostly a surface phenomenon. When light strikes a glossy surface, it is reflected so that the angle of reflection is equal to the angle of incidence. If the surface is rough, the reflected light will be at a different angle. An ideal dull or flat surface is one which is covered by a uniform and microscopic roughness so that light is reflected equally in all directions. Any powder which is uniformly distributed and in sufficient quantity will do this. For clear films, which must reveal such things as grain of wood, aluminum stearate is ideal. It has been found that for proper flatting there must be an optimum degree of dispersion. If the dispersion is too coarse, obviously the film will be undesirably rough. On the other hand, if the dispersion is too fine, the surface will not be rough enough or too smooth and glossy.

Let us see how the degree of dispersion affects the surface roughening or flatting effect. Dispersion is governed by several factors, such as, type of vehicle, efficiency of grinding and type of stearate. The formulator is in a position to choose the type of varnish or lacquer which will give him the best results. He should also know if his mills are grinding efficiently or not. When he comes to the choice of a stearate, he has several to choose from. In the first place, he should avoid overheating by water cooling his mills so that aluminum stearate can be used to give a transparent film. Then he should choose the grade of aluminum stearate which gives him the most flat with the least thickening. This is illustrated by Table IV, which shows a relationship between flatting

TABLE IV—Flatting

Grade	*Washed Ash*	*Free Fatty Acid*	*Gloss*	*Thickening*
Aluminum Stearate—				
V	6.0	30	110	(1)
XX	7.0	20	100	(2)
R	8.0	12	90	(3)
GM	9.0	6	80	(4)
Metasap 537	10.0	5	60	(5)

(1) Least; (2) Little; (3) Medium; (4) High; (5) Most.

effect and washed ash content and free fatty acid. It will be noted that more flatting is obtained as the washed ash is increased and the free fatty acid is decreased. However, the stearate which produces the best flat also produces the greatest thickening and possible seeding. Therefore, a compromise will have to be made in the choice of the right stearate.

Silk Screen Extender Base

Silk screen printing requires a special type of paint. It must have a very heavy body free of tackiness so that it may be sheared easily without smudging. In general these compositions have a high volatile content. Several metallic soaps are used to formulate this kind of composition. Although zinc palmitate and calcium stearate are used, aluminum stearate alone or a mixture of one part calcium stearate with two parts of aluminum stearate is most common.

Paint and Varnish Removers

It often happens that after a great deal of study and care to develop and apply a protective coating, it becomes necessary to remove paints or varnishes. Here again aluminum stearate offers a helping hand. It will thicken and retard the loss of solvents ordinarily used in these formulations to soften the unwanted film.

Let me conclude by saying that although the stearates are expensive and at times difficult to handle, they do help solve some of your most difficult problems.

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INFLUENCE OF THE ACID-HARDENING PERIOD OF PHENOL RESIN

By DR. FELIX WILBORN

It is well known that the acid-hardening varnishes produce films of outstanding atmospheric resistance among unpigmented varnishes, excelling even the most resistant oil varnishes in this respect. It is true that they are still offering a number of unsolved problems and that the solution of these problems is the more difficult since (1) the various products obtained may exhibit very different properties and (2) the varnish producers usually are not sufficiently informed as to the character of the resins employed in the manufacture of their products.

A series of important problems which, to my knowledge, have not found sufficient attention in scientific and manufacturing quarters are those surrounding *the period of acid-hardening*. For instance, is it more advantageous to apply fresh solutions of this type or to await partial condensation within the solution before application?

It is a matter of experience that freshly acidified phenol resin varnishes may under certain conditions fail to dry entirely.

The experiments reported on below are of a preliminary character only. They were conducted with two acid-hardening varnish mixtures. One of these, a pure phenol resin varnish, consisted of

Luphen-H (I.G.Farben)	100	parts by weight
Thinner	30	" " "

The other mixture, a mixed phenol resin-urea resin varnish, was composed as follows:—

Plastopal C B (I.G.Farben)	100	parts by weight
Luphen A T (I.G.Farben)	400	" " "

The latter varnish exhibits good drying properties. Since the character of the two components of this mixture does not appear to render them very suitable for acid-hardening varnishes, this property seems peculiar. However, it is entirely due to the selection of the optimum mixing ratio of its constituents. If this ratio is increased or decreased beyond a certain narrow range, badly or non-drying films are produced. The films of the mixed resin varnishes yellow but little and retain a fair degree of ductility, although they do not become nearly as hard as the films of the varnishes containing Luphen-H. If under the conditions of our experiments these films actually exhibited certain initial phenomena of decomposition—which, by the way, is also the case with the pure phenol resin varnishes—this is due entirely to the fact that this slowly hardening film is characterized by a certain degree of sensitiveness before finally reaching a sufficient stage of development—especially under the particularly unfavorable conditions of the initial time of exposure selected. Another reason was that phosphoric acid—such as used in our experiments—cannot be much recommended as catalyst for the purposes in question.

Nevertheless, the tests conducted by us yielded interesting experimental results, and it is a matter of experience that under practical conditions of application this varnish—employed as clear lacquer as well as a vehicle for paint mixtures—proved a highly useful material.

Three different types of catalysts were employed in the course of our experiments: a 60-percent solution of benzol sulfochloride and the Luphen-hardener-10 (I.G.Farben) of unknown chemical composition for the pure phenol resin varnish and a phosphoric acid catalyst of the following composition for the mixed resin varnish:

Phosphoric acid (spec. weight 1.4)	25	parts b.weight
Water	25	" "
Ethyl alcohol	50	" "
	100	parts b.weight

The samples of phenol resin varnish were mixed with 5 percent of the first two catalysts and were applied on the test panels after one, three and six days of storage. The mixtures could not be stored for a longer period than six days but required a certain period of ageing in order to ensure perfect drying.

The mixed varnish samples—which did not thicken as rapidly as the straight phenol resin varnishes—were mixed with two percent of the phosphoric acid catalyst and applied after one, three, six, twelve and fifteen days of storage.

Application of the varnishes was effected on pine-wood and hard fibre panels primed with one coat of the varnish containing 20 percent of thinner followed by two coats of the unthinned varnish.

The panels were exposed to outside atmospheres on January 27, 1942, i. e. eight to twenty days after application.

Results

On March 31, 1942 all phenol resin films still proved satisfactory, the conditions of the mixed varnish films being as follows:

Period of acidification	*Hard-fibre panels*	*Pine wood panels*
One day	mat	mat
Three days	mat	mat, craqueling
Six days	satisfactory	satisfactory and glossy
9, 12 and 15 days	mat, craqueling	mat, craqueling

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These results exhibit a clear optimum at six days of storage (acid-hardening) before application. A longer period of storage proved more unfavorable (under the conditions of test selected) than shorter periods of ageing.

On July 20, 1942 the tests had developed as follows:

Pure phenol resin varnish:

Hard-fibre panels: All films had acquired a duller, brownish appearance but were still satisfactory. Browning was most pronounced in the lacquers applied six days after storage. The varnishes containing Luphen hardener-10 had turned browner than those containing benzol sulphochloride.

Pine wood panels: Similar conditions prevailed, although the films containing benzol sulphochloride and exposed to six days of storage exhibited a few cracks in the annual rings of the wood panels.

Mixed varnish:

Hard-fibre panels: Craqueling had developed throughout, although the differences in appearance were not suffifficiently pronounced to be clearly definable.

Pine-wood panels: The individual films had developed more characteristic differences:

Period of acidification:	*Results*
1 day	no craqueling
3 days	commencing craqueling
6 days	dull, but satisfactory
9 days	rapid craqueling but only superficial (no downward penetration)
12 days	cracking along the annual rings of wood panels. Commencing loosening of films in sections of not longer than 1 millimeter.
15 days	craqueling, but apparently not down to the base surface.

On August 31, 1944 (i. e. after 31 months of exposure) the state of condition of the tests was as follows:—

Pure phenol resin varnish:

Hard-fibre panels: All films were brown and dull but satisfactory in all other respects. Browning was most pronounced in the films of the varnishes stored six days. The varnish films containing benzol sulpho-chloride had developed an equal degree of browning.

Pine-wood panels: These tests yielded results varying in a much higher degree, the most characteristic phenomena being as follows:

Period of acidification	*Catalyst*	*Results*
1 day	benzol sulphochloride	browning and dulling, otherwise almost in order
3 days	"	cracked off a little
6 days	"	loosening in the annual rings, partly cracked off
1 day	Luphen hardener 10	browning and dulling, otherwise almost in order
3 days	"	the same
6 days	"	film loose over large area but still adhering

(Attention must be called to the fact that in case of pronounced dulling of the films of this type craqueling is not visible.)

Mixed varnish films:

Hard-fibre panels

Period of acidification	*Results*
1 day	scaled off 70 percent
3 days	scaled off 85 percent
6 days	scaled off 30 percent
9 days	scaled off 80 percent
12 days	scaled off 30 percent
15 days	scaled off 70 percent

Pine-wood panels:

Period of acidification	*Results*
1 day	scaled off 20 percent
3 days, 6 days, 9 days, 12 days	scaled off 60 percent
15 days	scaled off 50 percent

Final Results of Our Experiments

(1) In the case of the pure phenol resin varnishes made from Luphen-H the weathering resistance of the films decreases—and the degree of browning increases—with the time of storage (period of acidification) previous to application. This applies to the varnishes containing both types of catalysts (benzol sulpho-chloride and Luphen hardener-10).

(2) The mixed resin varnishes obviously develop a clearly defined optimum range of storage periods. Storage periods of six days previous to application yield the most resistant films, although during the later stages of experiments these differences did not remain as clearly pronounced.

(3) The difference between the influence exerted by the two catalysts, benzol sulphochloride and Luphen hardener-10, need not be considered here since this problem did not form an object of this present investigation.

Conclusion:

It is obvious that the variety of problems involved and the general conditions in question are not sufficiently simple and one-sided to permit of the drawing of final conclusions on basis of the results obtained by the series of experiments forming the subject of this report. It is also clear that the various influences involved are too complicated to have been fully considered and evaluated within the scope of this investigation. However, it appears probable from the results obtained by us that in the case of the varnish mixtures selected by us short periods of storage are preferable, since paint materials of low molecular values—which tend to penetrate more deeply into the micropores of the wood—appear to be the most advantageous for the purposes in question.

On account of their lower degree of hardness and their lasting ductility, the films developed by

the mixed resin varnishes doubtlessly assume a special position.

It seems necessary for this reason to elucidate conditions more thoroughly by following up these experiments with other tests, but it appears from the results obtained by us that films of more satisfactory general properties are obtained by maintaining comparatively short periods of storage, by acidification, previous to the application of the varnishes, i. e. by permitting the catalysts to act only a sufficiently long time to ensure thorough drying of the films.

ALKYD RESIN TECHNOLOGY

By E. M. BEAVERS, The Rohm & Haas Company, Philadelphia

Our objective, in this discussion of alkyd resins, is to correlate their chemical make-up with their physical properties and their uses.

Alkyd resins are polymeric esters prepared from polyhydric alcohols and polybasic acids. The chemistry of their formation, therefore, reduces to one of the simplest of organic reactions—esterification.

The first alkyd ever described in the literature was made by Berzelius, in 1847, from tartaric acid and glycerine. The reaction of succinic acid and glycerine, to give a gelled, insoluble mass, was carried out by von Bemmelen in 1856. Watson Smith, in England, reported a glyceryl phthalate product in 1901.

A sytematic search for uses for glyceryl phthalate was made by Callahan from about 1910 to 1915 in the General Electric laboratories, and several patents ensued from this work.

Great impetus to work in this field came from the development of the Gibbs and Conover process for the manufacture of phthalic anhydride by the oxidation of naphthalene, in 1918. This markedly improved the commercial attractiveness of products based on phthalic anhydride, which formerly had been a relatively rare and expensive chemical. By 1920, patents had appeared under the names of Arsem, Howell, Dawson, and others, describing glyceryl phthalate resins modified with oleic acid and castor oil.

In the late twenties, a number of people had the idea of embodying fatty acids from fast-drying oils in alkyds. Although a patent on this concept was granted to Kienle, it was later invalidated, and many companies entered the field. The growth of alkyd production has since been rapid indeed.

It was also in the late twenties that the chemistry of alkyd manufacture was clearly understood for the first time, largely as the result of work by Carothers and by Kienle.

When one reacts methanol with acetic acid, the products are the small molecule methyl acetate and water. To drive the reaction to completion, one must remove the water as it forms. If ethylene glycol, with two hydroxyl groups, is reacted with acetic acid, the product is ethylene diacetate, which to the polymer chemist is still a small molecule.

However, if ethylene glycol be reacted with phthalic acid (having two carboxyl groups), hydroxyl and carboxyl groups remaining on the ends of the small molecules first produced can continue to react with each other. The result is that the molecule steadily grows to a long, threadlike polymer as esterificatin continues. No matter how far the reaction is carried, the linear polyester remains fusible and soluble.

When glycerine, a tryhydric alcohol, is used with phthalic anhydride, the result is essentially the same, except that polymer branches can now grow from the third hydroxyl group. If reaction is continued long enough, the molecules may become so large and complex that gelation occurs; i. e., the product can be converted to an insoluble and infusible form.

When a monobasic acid, such as acetic or oleic, is used along with the glycerine and phthalic anhydride, the effect is to reduce the amount of polymer branching that can occur. If one mole of monobasic acid is employed for every mole of glycerine, then the monoglyceride will behave like a glycol of only two hydroxyl groups, and essentially linear polymers will be produced by reaction with the phthalic.

The foregoing generalized picture is indicative of the type of raw-materials used in making the vast majojrity of conventional alkyds. Glycerine is the polyhydric alcohol used in most instances and in largest quantity. Pentaerythritol is also used to a lesser extent, and this polyhydric alcohol has both advantages and disadvantages by comparison to glycerine. Pentaerythritol alkyds are usually faster drying and more resistant to alkali, while glycerine alkyds usually have better stability, adhesion, and compatibility with other film-formers.

Ethylene and propylene glycols, and their polyether glycols, are commercially available at low cost, and are used to some extent in alkyds, principally in those of the linear type.

Of the dibasic acids available, phthalic anhydride is used in largest volume. Much smaller

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Paper presented at the Twenty-Second Annual Convention of the Association of American Soap and Glycerine Producers, Inc., at the Commodore Hotel, New York.

amounts of maleic and fumaric acids are used, although the supply and demand for maleic seem to be growing rapidly. Adipic and sebacic acids are relatively long-chain, aliphatic, dibasic acids which give "softer," more flexible alkyds than does phthalic anhydride.

The monobasic acids are derived from natural fats and oils, in which they are found as the triglycerides. The most common fatty acids in nature are stearic, oleic, linoleic, and linolenic acids. These are all eighteen-carbon acids having, respectively, zero, one, two, and three double bonds per molecule. In the acids of multiple unsaturation, the double bonds are separated by methylene groups and are not conjugated. Various amounts of these acids are found as mixed glycerides in soyabean, cottonseed, corn, peanut, olive, and linseed oils. The property of air-drying begins to be observed when the oil contains an average of about 1.5 double bonds per fatty-acid unit.

The major constituent of tung oil, also called chinawood oil, is the glyceride of eleaostearic acid, which contains three double bonds. These bonds are all conjugated, and tung is one of the fastest drying oils known.

Castor oil contains a large proportion of the glycerides of ricinoleic acid. This unusual acid has one double bond (thus, the oil is not air-drying) and one hydroxyl group. The high viscosity and lubricating and purgative properties of castor oil are due to this hydroxyl group. The acid can be dehydrated to give a doubly unsaturated product whose glyceride is air-drying.

We have seen how the proportion of monobasic, fatty acid combined in the alkyd can be varied regularly from none to the oil with no glyceryl phthalate component. The physical properties of the products depend upon the ratio of glyceryl phthalate (or other polyester) to fatty acid chosen. The proportion of glyceryl phthalate in the product is sometimes spoken of as the "alkyd ratio." Thus, the alkyd ratio of pure glyceryl phthalate (the upper limit of the scale) is 100. The alkyd ratio of a pure oil is zero (the lower limit of the scale).

Limiting our attention for the moment to alkyds based on glycerine, phthalic anhydride, and drying oils, we may relate the alkyd ratio to properties and uses of the resins.

Glyceryl phthalate has found little practical use. The highest alkyd ratio ordinarily found in commercial products is about 65. Here, viscosity is very high, and strong, aromatic solvents are required. These alkyds are used as hardeners for other alkyds of higher oil content, and have some advantages over urea-formaldehyde and nitrocellulose hardeners, detracting less from adhesion and flexibility.

At alkyd ratios of about 50, the so-called "short oil" alkyds are produced. Viscosity is still high, and these also require aromatic solvents. The resins are used as vehicles for baked coatings for such articles as Venetian blinds, metal cabinets, cans and caps, and automobiles.

When the alkyd ratio is reduced to about 40, the products are lower in viscosity, and solubility in aliphatic solvents is now realized. These alkyds are usually applied by roller-coating or spraying, and find wide application in air drying pigmented

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enamels, maintenance paints, metal decorating, auto and truck refinishing, and sign painting.

At alkyd ratios of about 30, viscosity is still lower, and the enamels are well adapted to brushing. They are used as architectural finishes, as coatings of high flexibility (for toothpaste tubes, for example) and as trim and trellis paints. The high durability of this type of alkyd was of particular value for marine finishes during the last war.

Alkyds employing non-drying fatty acids also find important usage. These resins are usually based on raw castor oil or coconut oil, and have alkyd ratios of 50 to 65. They are used as plasticizers for urea or melamine resins and for nitrocellulose. Their color and color retention are excellent, which adapts them to the high-quality finishing of refrigerators, stoves, and washing machines.

The "soft" alkyds prepared from aliphatic dibasic acids such as sebacic and adipic have been used as plasticizers and as the vehicles for caulking compounds. If drying oils are also used with these acids, flexible, durable coatings are possible for fabrics, rubber articles, and cables.

It was found during the war that linear polyesters, made solely from dibasic acids and glycols, are compatible with a wide variety of plastics. They have shown special value as plasticizers, for polyvinyl chloride and chloride-acetate copolymers. As plasticizers, the polyesters have the advantages of extremely low volatility and migratability, high resistance to water and solvents, excellent stability under ultraviolet light and at elevated temperatures, and improvements in some processing characteristics. The first large-scale exploitation of these properties was in an improved jacket for radar cables. The feature of low volatility is of particular importance in free films with polyvinyl chloride, found in handbags, shoes, furniture, upholstery, luggage, etc.

A new type of laminating resin has appeared in recent years, consisting primarily of solutions of unsaturated, linear polyesters in vinyl monomers. These have become known as "contact resins" because only contact pressure with the mold is necessary in curing the resin. The polyester component contains unsaturation introduced by maleic or fumaric acid, for example, and during the cure is therefor capable of copolymerization with vinyl monomer. The latter is styrene in most cases. The curing operation is accelerated by peroxide catalysts, and even faster auxiliary catalysts have recently appeared.

The most promising applications for the contact resins seem to be flat laminates for drain-boards and table and cabinet tops; colorful, washable, wall coverings; "potting" of electrical equipment, such as condensers; and casting of innumerable articles. The toughness and flexibility of contact resins laminates adapts them particularly for bus and train installations.

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The alkyd field is continuing to grow. In 1947, nearly 300 million pounds of ester resins were produced, and 1948 undoubtedly saw this figure exceeded. Aggressive research in this field, versatility of the chemical system, and alert development of new markets assure its future health.

STYRENATED ALKYDS

WAYNE C .NORRIS, Stamford Laboratories of the American Cyanamid Company

Styrene became of age in the surface coatings industry during 1948. Whatever the future may hold for it in our field, it was the past year that marked the first extensive use of styrene with drying oils and their derivatives. Styrenated alkyds made their appearance during 1948 and it may be said that they have already found their way into many formulations and applications to which they are peculiarly and outstandingly well adapted.

Since styrene and polystyrene have been with us for such a long time the question might well be asked—why did it take so long to utilize them in surface coatings? While it is not our intention in this short treatment to go into the subject historically, it might be well to point out one or two approaches to the problem which were made in the past.

The formation of polystyrene as such, and the subsequent attempts to modify it with or add it to oils or other film formers did not meet with much success, although such products were announced almost ten years ago. Even though the merits of styrene were made apparent, these offerings generally suffered on the one hand from too low a molecular weight, resulting in a spewing, plasticizing type of resin, or were of too high a molecular weight to insure sufficient compatibility with other film materials. It must be admitted, however, that these polymers ran into W.P.B. General Allocation Order M-300 and even had they been of exceptional merit would have had to wait until the end of the war for full exploitation.

In 1942, Hewitt and Armitage of England entered the picture by copolymerizing styrene with unsaturated drying oils and alkyds. Although promising results were obtained, these products suffered from at least some of the following characteristics: in manufacture they required long reaction times, had low conversion values, and reaction conditions were extremely critical; the solutions were cloudy and required strong solvents, they contained a high percentage of monomeric styrene and had poor flow and pigment wetting properties. Patents were later obtained which claimed to overcome some of these disadvantages, but meticulous adherence to their teachings failed to yield styrenated alkyds satisfactory either to produce or market in this country.

Paper presented at the thirteenth annual convention of the Southern Paint and Varnish Production Club, in Biloxi, Miss., March 9-11, 1949. This paper will be published in a later issue of the Official Digest.

That most if not all of these difficulties were solved in this country is attested by the successful introduction during the past year of styrenated alkyds in both xylol and mineral spirits solutions. In general, these new resins offer the Surface Coatings Industry fast drying or curing films with excellent gloss, good water and chemical resistance at a cost no higher and potentially lower than that of a pure oil-modified alkyd. More specific description requires that we discuss particular products and since we know most about the Cycopol resins we will confine our observations to such of those as have already appeared or are about to appear on the market.

Cycopol is Cyanamid's trade mark representative of a new line of polymeric or co-polymeric resins designed especially for surface coatings. Cycopol S 101-1 was the first of this line; the *S* meaning styrene type and the 101-1 meaning that this first resin was in petroleum spirits solution. It is still the only styrenated phthalic-alkyd available to the trade in mineral spirits solution.

This fact in itself illustrates a degree of stability and applicability not heretofore attained in such products. The only recommendation made on further thinning is that the Kauri Butanol value of the reducing solvent have a minimum value of 40. Enamels prepared from Cycopol S 101-1 will air dry tack free in from 1 to 2½ hours and dry hard in 3 to 4 hours with the driers normally used for pure alkyds. Baking times are correspondingly fast and the films whether air dried or baked are characterized by very good gloss retention.

Even though gloss and gloss retention are characteristic of Cycopol S 101 it is still desirable that a certain amount of care be exercised in pigmentation because there is evidence that the inherent wetting power of styrenated alkyds is not as good as that of a good alkyd. Fortunately, however, this is of significance only with pigments which are more difficult to wet and even with these it is possible to achieve excellent results with only moderate attention given to good formulating practice.

Another Problem

In many respects baked films of these resins can be considered as intermediate in properties between those of alkyds and alkyd-amino films. This applies to hardness, water, acid, alkali and soap resistance. Although their resistance to

hydrocarbon solvents and their mar-resistance are adequate for many applications, they are not equivalent to a well-cured alkyd-amino resin combination. Needless to say, research workers in this field are giving their attention to these problems together with those of impact and abrasion resistance and definite progress is being made. Surprisingly, however, the adhesion of Cycopol S 101-1 is so good that a mixture of 70 parts (solid basis) with 30 parts Melmac 248-8 constitutes our best recommendation today for a single bake finish without primer over Bonderized steel for washing machine enamels. It was to be expected that this combination would be superior in soap resistance to the normal alkyd-amino combination; repeated tests have also shown it to be superior in gloss, color, hardness and practically equal in abrasion and impact resistance.

Not enough time has elapsed to have the whole story on durability, however, the following facts can be reported. As with all new products our first exposures were clears on bare steel. Air dried films of Cycopol S 101 were fully equal in out-door weathering characteristics (at Stamford, Connecticut) to the pure oil modified Rezyl 435 and much superior to the rosin modified Rezyl 729 after six months.

Difficult To Draw Conclusions

It has been difficult to draw any clear-cut conclusions from accelerated weathering exposures. Baked panels have consistently weather better than air dry panels and in many cases are fully equal to the resistance of a pure oil modified alkyd. Failure, when it appears, is of the checking type, but since no failure other than some loss of gloss and color has occurred on exterior exposures of Cycopol S 101 enamels after upwards of 1 year, we feel that checking under accelerated weathering is possibly but a mild symptom and not portentous of a serious defect. These outdoor exposures are on both the Stamford and Florida test fences in a variety of enamels both air dried and baked. Certainly more time is needed to develop the whole story of durability. To summarize conservatively on the data so far developed; it appears that Cycopol S 101-1 has good exterior durability and that baked films are superior to those air dried. Incidentally, there is little question of its superior durability in comparison with the styrenated oils so far examined.

To satisfy the demand for a still faster air drying product than Cycopol S 101-1, we are glad to be able to announce today a new product, Cycopol S 102-5. As the coding indicates, this is also a styrene modified type with the -5 showing that it is a xylol solution. It will be offered as a 60 per cent solution in mineral spirits of Cycopol S 101-1. It truly approaches lacquer in speed of air dry and like Cycopol S 101-1 it also may be baked. In addition to drying much faster and curing harder than Cycopol S 101-1, Cycopol S 102-5 has even better color, gloss and chemical resistance. As might be expected it is not as good in flexibility or impact resistance and its exterior durability

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may not be as good. Having such fast air drying properties and being cut in xylol, it is not so versatile for a grinding medium as Cycopol S 101-1, although satisfactory enamels have been prepared in all colors. For example, it is preferred to grind blacks in steel ball mills and it may be advisable for some colors that the grinding be done in Cycopol S 101-1 and the reduction with Cycopol S 102-5.

Compatibility Limited

As with all styrenated alkyds the compatibility of Cycopol S 102-5 with other film forming materials is somewhat limited, with S 101-1 being the better in this respect. They will accept refined or light bodied oils in amounts at least as high as 10 per cent which permits tinting whites with stock pastes of color in oil. There is little point in adding most of the other film formers with the exception of Beetle and Melmac resins. All types of these two amino resins are completely compatible within the ranges that would normally be used and some of the advantages to be gained by using Melmac 248 and Cycopol S 101 have already been pointed out.

Analysis of styrenated alkyds has proven to be a problem for our Analytical Division. However, it is our intention to keep you up-to-date on such work in order to facilitate your cooperation with governmental and other agencies where complete specifications are demanded. For phthalic anhydride determinations, we find that only a minor modification of the Kappelmeier method is necessary to yield consistent and accurate results. Determination of fatty acid content is quite another matter because of the tenacity of the bond between polystyrene and the fatty acid complexes. In addition, there is an appreciable percentage of unsaponifiable material consisting mainly of polystyrene or perhaps large quantities of it copolymerized with a small quantity of fatty acids. While much remains to be done in developing reliable methods of analysis we are ready and willing to give you the benefit of our available information as you need it in attempting to meet present specifications or in the preparation of new ones.

We do not believe by any means that the styrenated alkyds are the panacea for all ills of the coating industry. We do believe, however, that they constitute a distinct contribution and have certainly broadened the vista of surface coating research personnel. We hear more and more talk of chain initiators, propagators and terminators; conversion rates, etc.; whereas such expressions as "holding for a 4 inch string" or a "clear hard pill" are becoming echoes from a distant but interesting past. The uses to which the products are being put are, however, quite familiar to you and include coatings for farm equipment, machinery, implements, toys, washing machines, and for fast dry trade sales products.

We are currently and actively engaged in the further improvement of reactive monomer modified alkyds and are confident that the sales of the products already on the market and those about to appear, will more than justify the continued research and development necessary to keep you ahead in producing quality products at a profit.

"BLUE PRINT IN ACTION"

By JOSEPH A. HAGER, Vice-President, Grand Rapids Varnish Corporation, Grand Rapids, Mich.

Yes, the "Blueprint for Action" has become the "Blueprint in Action." The year that has passed since the presentation of this plan at our Atlantic City convention has seen continuing discussions, refinements, and clarifications of it, and the activation of special study groups as recommended by it. Some of these groups have already completed their initial study of their assigned subject.

The year's work, however, has made very clear, one fact. Too few members of the Association understand the plan, its objectives, or the methods by which it is proposed to achieve them. It is for this reason that I believe that it is desirable that we have a clear explanation of the plan and the method which is recommended for its utilization.

What is a blueprint for action? Basically, it is a long-range plan that seeks to further the best interests of our industry through clarifying and defining our objectives, through elevating our standards, and through improving and expanding our knowledge, this through the unison of group effort, further through such group effort to attempt to achieve agreements on and subscription to details, to desirable and beneficial industry objectives in research, formation, production, sales and management.

The blueprint for action is just what its name implies. It is a drawing that seeks to break down the whole of our problems into component parts to permit intelligent and exhaustive study of each component and its relationship to the whole. It is a plan of action that will benefit all of us but until it becomes the blueprint in action, it is of little value.

Why the blueprint for action? Simply because of clearly and repeatedly indicated need for its

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Address at the 60th annual convention of the National Paint, Varnish and Lacquer Association, in Chicago, November, 1948.

objectives and because whatever its shortcoming, no better plan has been advanced to date.

What benefits can the blueprint possibly bring to you? Well, that is for you, and you individually, to determine. Depending upon the degree of your acceptance of it and your participation in it, the reward in benefits to you will be proportionately great or small.

How can the blueprint be put to work and utilized? Well, gentlemen, there is only one way, and that is by our rising above our selfish interests and subscribing to the belief that that which is for the greatest good of the greatest number must prove to be for the greatest good of the individual. Maybe you can't embrace that ideology; maybe you can.

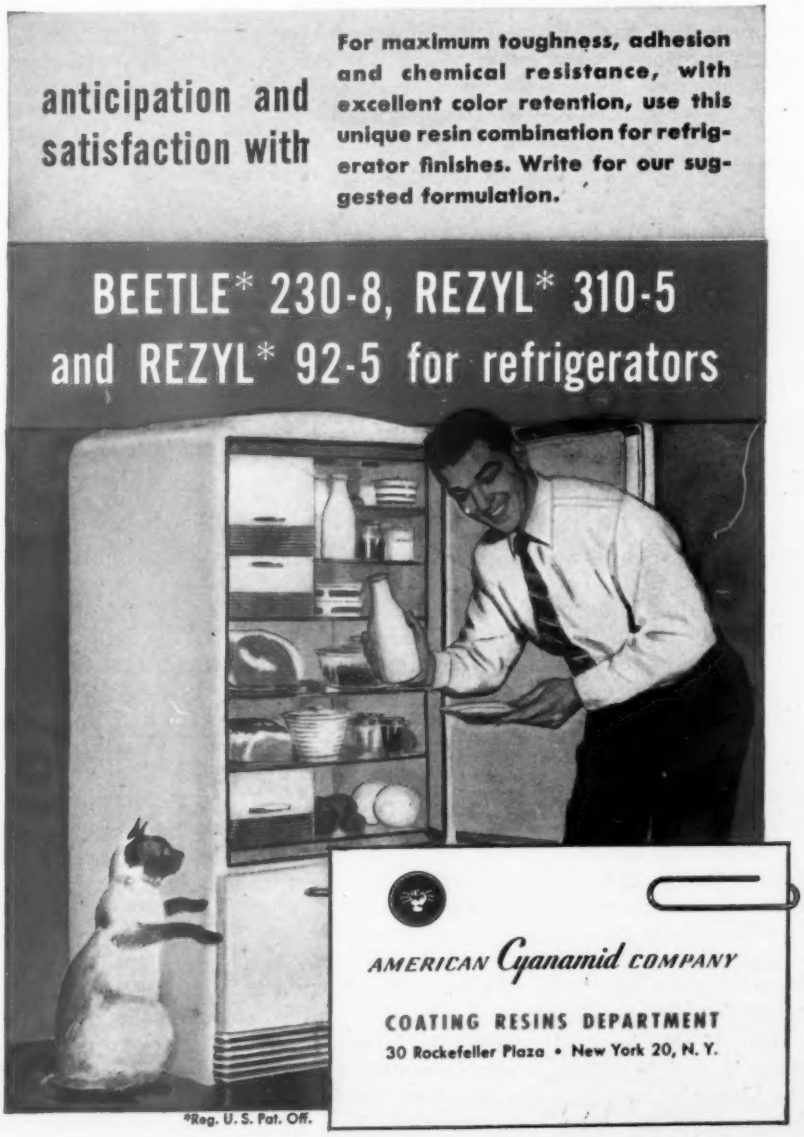
Basically, the blueprint is a search for the truth, but because who is there among us that knows the truth, maybe we should say it is a search for the good, for the good of all of us. The blueprint seeks to determine the good through the means of group studies of every facet of our common problems.

For example, in the blueprint, a set of related subjects are grouped together under a common heading as, for example, interests of the end user. Naturally falling in this category is a subject such as public relations, the relations existing between us, as manufacturers of industrial finishes, and the ultimate consumer of the product on which those finishes are used. You will recognize that there is a long chain between the two. There is the manufacturer using our product and the distributor and retailer of his product.

Is it far-fetched for us to be concerned with the relationships existing between ourselves and such end users? Maybe yes. Maybe no. But it is the purpose of the blueprint to find out by developing, defining, clarifying those interests and setting forth ways and means whereby we can better serve them to the mutual profit and advantage of everyone connected with the same.

Attempting such a group study, regardless of the topic, so long as it be one of genuine interest, must as you can realize result in an unusual exchange of ideas. This exchange of ideas can but result in a better understanding and this better understanding cannot fail but produce important definitions and clarifications of our objectives, cannot fail to elevate our standards, and cannot fail but to promote improved and expanded knowledge.

All of these, you will admit, are sorely needed by our industry but, further and above these valuable benefits, such group study provides bonus payments to those engaged therein. These bonus payments will result from the benefits accruing to the individual, from the new and/or accrued association which he makes, from the new and/or improved understanding which he gets, and from the stimuli and broadened vision that result from a broadened concept.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Search for the Good

I have said, basically, the blueprint for action is a search for the good. You may question, and rightly so, that the industry can agree upon what is the good. You may say, "What is good for you may be very bad for me," and you may well be right.

Certainly there are many illustrations that ostensibly prove the point. For example, so simple an occurrence as rain may prove to be a bonanza for the farmers in a moisture-starved farm area, but at the same time may bring great financial loss to sports promoters operating in that area. A landlord's idea or definition of a good child may well be one who stays in bed all day, but a parent's may vary from a docile, obedient, well mannered child, to one who shows its resourcefulness and its self-sufficiency, perhaps even to the point of taking issue with the parent on a matter in dispute.

I could give you many similar illustrations of the prevailing class of opinions on the subject: what is the good? You yourself can think of an endless number. This wide diversity of personal interest, hence the widely resulting differing opinions on the subject of what is the good, is the basis of all of our progress today.

What Is the Good?

It prevails in the relationships in our own family, between ourselves and our neighbor, our fellow townsmen, our business associates, and our competitors. It exists between our state and neighboring states, our country and neighboring countries, yes even in our respective religions.

If we look back, we become aware of an intensification of and a widening of the distances between our definition of what is the good and our acceptance of other definitions.

Why has this been so? Well, my opinion—and it is solely my opinion—is that it results from, first, a too rapid advance in scientific knowledge; and second, a too rapid increase in population, both resulting in an acceleration of the tempo of living that has left us hopelessly behind.

I will not expand on this subject, on this phase of this subject, for I introduce it solely to spotlight the fact that of necessity there exists widely divergent views on the question: what is good? And we must take this fact into consideration when we plan and chart an activity like the blueprint in action.

There may be among you some who honestly believe that your individual interests are so unlike those of the industry that it would be a most forlorn hope to attempt to ever resolve the two. And you may be right. Maybe the blueprint for action is on the scene too early. Maybe the industry isn't ready for it.

But, if that be so, it won't take long to determine it, and it will be a simple matter to shelve the blueprint, pending the time that the industry becomes mature enough to undertake it.

It Can't Be Done

But lest we be tempted to hopelessly shrug our shoulders and say "It can't be done, our industry was built on sharp practice, on keen competition, but I can't hope to succeed except as an individualist of the most outstanding kind by taking everything he can from industry-wide efforts and giving a little in return," let me recommend to you some serious thinking along this line. Isn't it true that those vocations and those firms and those industries that believe that way are always the ones in which monetary reward for their labors and their efforts is at the minimum? And isn't it true that as a firm grows in size and in importance, it begins to think more and more in terms of generally accepted business practices and methods? Do you see the giants, the so-called giants of American industry, operate on the level of a pushcart vender?

You know! You know from the way they operate, from the way they serve their customers, their stock-holders, and their employes and from their great financial strength and ability, that they have found a way of resolving their individual opinions into a working formula that they all can and do subscribe to.

Everyone Benefitted

As a reward for this accomplishment, everyone connected with those industries or served by them is benefited in a manner that is possible only in our fine country.

Here then is the blueprint for action approach to the problem of resolving our differences of opinion into a working formula that each of us can and will subscribe to. Each of the six club committees of the Steering Committee of the Industrial Finishes Division of our National Association, working with the Industrial Finishes Committees of local clubs, arranges for the formulation of specialized study groups for the purpose of thoroughly studying an assigned subject. This same subject is then assigned to four or more local associations.

This will insure consideration of the various viewpoints that result from geographical location, from specialized products, and from local conditions and problems. These study groups generally consist of from six to twelve men whose jobs with their respective companies best fit them to study the subject assigned.

This conclusion in the form of a paper or a report is presented to the subcommittee that arranged for the study. When the reports of all the committees are received, the National Subcommittee draws up a combined or a consolidated report based on these various papers. This report is then presented to the Steering Committee who, after approving it, arrange for industrywide distribution.

A year ago, the blueprint for action was on trial. It was just a plan. We believed that it would produce worthwhile results and that those who en-

gaged in it would be benefited, but we had no proof.

Today, we have proof, proof that the group studies make valuable contributions to our knowledge and our thinking, but more important, proof that the individuals engaged in those studies are generously rewarded.

Two clubs, the Detroit and the Cleveland Paint and Lacquer Associations, have already undertaken and completed such group studies. They chose as their study, that of selling quality finishes towards elevating and improving customer relations. Each developed a paper on the subject, setting forth and expounding their ideas and their beliefs. These papers were presented at the last meeting of our National Steering Committee at the Sky Club.

Results of Study

The results of their study of what is of real value, was clearly attested to by General Battley, the President, and Ed Hoffman, Director of Industrial Finishes Committee of our National Association. I would like to read to you excerpts from these letters.

From General Joe: "These excellent reports indicate a splendid spirit of cooperation on the part of those who have participated in the study of this subject. These reports are so informative that I am forwarding copies to our advertising agency, Young & Rubicam, for consideration in connection with their efforts of organizing the industry's advertising campaign in this matter."

To J. L. Adams he says: "This project, sponsored by the Steering Committee of the Industrial Finishes Division, has, as you will note, resulted in excellent information on selling quality finishes. These studies merit special consideration because each report represents special effort of a local committee composed principally of salesmen of both large and small companies having plants in the area."

From Mr. Hoffman: "The reports are most interesting and informative and the subject appears to be very thoroughly covered as a result of the effort, time and study given by the members of the local committee." That those participating in the study were generously rewarded for their contributions of time and effort is proven, as you see from Clarence Kruger, President of the Detroit Club, and H. S. Sherman, Chairman of the Industrial Finishes Committee of the Cleveland Club. I would like to read to you excerpts from those letters. From Clarence Kruger: "It was our extreme pleasure to have had an opportunity to submit as the Detroit contribution, our ideas on this particular subject. The Industrial Sales Committeemen, who so graciously contributed of both their time and effort in the preparation of this paper, feel they have been rewarded and they have a much clearer understanding of what a quality finish really is. We have all enjoyed working together on this particular project. Perhaps, in the not too distant future, we will again be privileged to work on some other phase of the entire blueprint for action."

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And, from Mr. Sherman: "Your letter, I am sure, will encourage an attendance at future meetings. At present and as you know, we are standing by, awaiting further assignments. The important portion of these letters, the convincing proof of the value and the worth of the blueprint is the statement that these clubs await the opportunity of undertaking further work on the plan. They, more than anyone else, have had the opportunity of investigating the plan and judging its value to themselves as a group and as individuals. The very fact that they request and hope for additional assignments is all the proof that anyone could ask as to the value and merits of the plan."

In addition to these two clubs, others are at work. The New York Paint, Varnish and Lacquer Association has set up a committee under the able leadership of M. H. Horgman of the Standard Varnish Works. The St. Louis Club has G. R. Sangluss, President of the Sangluss Paint and Varnish Company, as Chairman of their group. Harry Shafer of the Shafer Paint and Varnish Company of Louisville, is the Chairman of their Committee. John C. Moore, who is Chairman of the National Scientific Section, is directing a committee on the subject of new raw materials, which it is anticipated will be completed by the year's end, and Harry Stone has made a preliminary report as Chairman of the Philadelphia Committee.

It is reasonable to think, therefore, that soon after the turn of the year, our National Association will be in a position to publicize the findings of these study groups. As can be appreciated, our present efforts have, of necessity, been along the line of a plan of operation. Practical problems attending the placing of a blueprint in action have had to be faced and solved. This is being done, and soon the tempo of the entire effort will be dramatically increased.

You, each of you, can make a valuable contribution to this work by interesting yourselves in and by participating in its development. It should be of particular interest to the officers of local clubs and to the chairmen of their Industrial Finishes Committees, for it provides excellent material for a program of activity that will capture and hold the interest of your members. So, don't sit back. Don't wait for an assignment. Rather, contact the Steering Committee and arrange for your participation and for the full details as to how you can become a part of the blueprint in action.

IMMEDIATE MEDICAL ATTENTION IMPORTANT IN CASES OF SOLVENT ILLNESS

Workers handling volatile solvents should be instructed to report promptly any feeling of discomfort. Dizziness, headache, eye difficulties, weakness, nausea, or stomach upset may be due to other causes, but they can also result from inhaling solvent vapors and may serve as an early warning that medical attention is required. Neglect of such warnings may lead to serious illness. Prompt medical attention, on the other hand, generally leads to complete recovery.

In one instance, a man spent several hours cleaning some equipment with a substantial quantity of solvent in a basement room where there was little ventilation. Several times he felt a little dizzy and went outdoors for a few breaths of air and to get away from the odor. Since this made him feel better he said nothing about his discomfort but kept at the job until it was finished. The next day he felt much worse and by the time he consulted a doctor he was seriously ill and had to be sent to the hospital.

In another case, a man entered a solvent tank to clean it, and made the serious error of entering the tank without a respirator. He became ill from the heavy solvent fumes and, instead of reporting to a physician, tried to treat himself by taking a few nips of hard liquor. A doctor would have told him that alcohol intensifies the effects of solvents on the body. His self-treatment led to serious illness.

Some persons are especially susceptible to solvent illness, and even a rather mild exposure (degreasing a motor or wiping metal parts with a solvent-saturated cloth, etc.) may lead to illness. For this reason, early signs of discomfort should not be overlooked even when it seems unlikely that much solvent has been inhaled.

While inhalation of solvent vapors is the most frequent source of solvent illness, it sometimes happens that the liquid is swallowed by mistake. The person should be made to vomit and a physician should be called at once. Also, since skin contact with solvent sometimes leads to dermatitis, persons who develop skin difficulties after working with these liquids should report to a physician to prevent aggravation of their condition.—Safety Research Institute, Inc.

The formation of a New Product Development Department was announced today by the American Cyanamid Company. One of the functions of the new department will be to determine whether there are economic uses for selected products which have been developed in Cyanamid's research laboratories, for which sales applications are not yet established. At present, most of the group's activity will be devoted to the evaluation of organic nitrogen compounds, although eventually the entire range of American Cyanamid's products will be included.

In addition to market development, the group will conduct market research on currently manufactured products, as well as those in the development stage.

RECENT ADVANCES IN PAINT TECHNOLOGY

CORRELATION OF STABILITY WITH FATTY ACID COMPOSITION OF HYDROGENATED VEGETABLE OIL. Cottonseed, peanut, and linseed oils were hydrogenated under selective and nonselective conditions and samples withdrawn periodically for determination of their fatty acid composition, keeping quality, and other characteristics. The results were submitted to graphical and statistical analysis from which various conclusions were drawn. G. S. Fisher, W. G. Bickford and F. G. Dollear. J. Am. Oil Chemists' Soc. **24**, 379-82 (1947).

FATTY ACID COMPOSITION OF HYDROGENATED VEGETABLE OILS. The fatty acid compositions of a number of unhydrogenated and hydrogenated peanut, cottonseed, soybean, and linseed oils have been calculated from the iodine number, thiocyanogen number, ultraviolet absorption after alkali-isomerization, and the content of saturated acids determined by a modified Bertram oxidation method. Analysis of the results leads to several conclusions. G. S. Fisher, R. T. O'Connor and F. G. Dollear. J. Am. Oil Chemists' Soc. **24**, 382-7 (1947).

IMPROVEMENT OF THE ADHESION OF ENAMEL TO CAST IRON. Experiments are reported which show that borax-containing enamels adhere better than the wartime boron-free enamels. By the addition of sodium silicotitanate and reduction of the quartz content, the adhesiveness of the enamel could be improved, even to the point where it was superior to that of the borax-containing enamels. Testing was by comparison tests. O. Kruger. Emailwaren-Ind. **21**, 59-61 (1944) (Abstr. through Chem. Abs. **41**, 7070 (1947)).

EXAMINATION OF PAINT MATERIALS. Four maleic resins and two phenolic resins of different manufacture were compared. Maleic resins have generally higher softening points; all acid numbers are approximately 20; alcohol tolerance of toluene solutions is equal; maleic resins have higher viscosities than phenolic resins in toluene solution, but for resins of equal softening point phenolic resins have higher viscosities. Used in conventional nitrocellulose lacquers maleic resins are much better in light-fastness, poorer in through-drying properties and somewhat poorer in extensibility; there is no difference in filling properties, color, hardness, polishing properties, resistance to whitening on mechanical damage and to water, aqueous sodium carbonate and aqueous alcohol. F. J. Hermann. Centraal Inst. Materiaal Onderzoek Afdel. Verf. Circ. **35**, 1-6 (1947) (Abstr. through Chem. Abs. **41**, 7137 (1947)).

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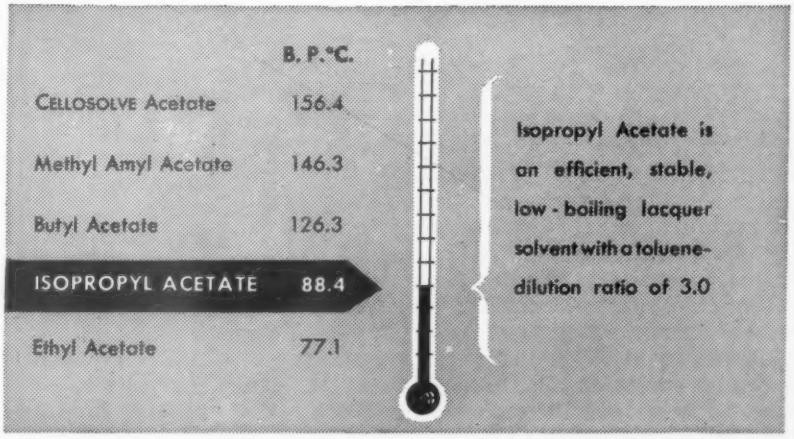
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FOREIGN PATENT DEVELOPMENTS

PRODUCING SILICON ALKYL HALIDES. J. Levy and Rotax, Ltd. Brit. Pat. 596,800. Applied for: Mar. 20, 1945; accepted Jan. 12, 1948. Silicon alkyl halides, useful in the production of insulating varnishes for the components of various forms of electrical apparatus, are produced by heating a gaseous or liquid paraffin such as methane with a silicon tetrahalide (e.g. silicon tetrachloride) or a mixture of silicon and chlorine, in the presence of a catalyst such as pumice or brick fragments or a palladium or platinum sponge.

PROCESS FOR REFINING GLYCERIDE OILS AND FATS. H. K. Allbright. Brit. Pat. 586,871. Applied for: Mar. 9, 1945 (applied for in U. S. Apr. 15, 1943); accepted Jan. 13, 1948. Crude vegetable glyceride oils containing as impurities free fatty acids, non-fatty colloidal impurities and coloring matter, are refined by treatment with alkali to neutralize the crude oil in the presence of alcohol, removing the impurities in the foots and washing and drying the neutralized oil. Emulsification of the neutral oil is avoided and the impurities are conditioned for separation from the neutral oil in the liquid state by treating the oil in the neutralizing step at 60° to 150°F. with dilute aqueous caustic alkali in quantity just sufficient to saponify the free fatty acids, and to solvate the non-fatty impurities and a substantial part of the coloring matter and the products of their reaction with alkali but insufficient to salt out the saponified product, thereby conditioning the mixture to have liquid foots and then separating the foots from the neutralized oil.

PRODUCTION OF SYNTHETIC RESINS AND STOVING ENAMELS. D. H. Finn, S. R. Finn, E. W. Lanfear and R. M. A. Welchman. Brit. Pat. 597,034. Applied for: Sept. 21, 1944; accepted Jan. 16, 1948. Synthetic resins and corrosion resistant stoving enamels especially useful for protecting weapons and weapon interiors from the powerful corrosive effect of chemical warfare agents, are made by effecting slow, controlled condensation under reflux conditions of approximately equimolecular proportions of phenol and aqueous formaldehyde in several increasing temperature stages—the temperature in the final stage being at least 70° and not over 95.2°C.—the time and temperature in the latter stage being coordinated so as to obtain the maximum possible uniformity in the rate of reaction (as shown by the absence of pinholing on stoving), using from 0.6 to 1.6% of alkali metal hydroxide (calculated on the weight of the batch) as catalyst, terminating the reaction when a separation of from 18-23% by volume of water is shown on salting out and centrifuging a sample portion and then salting out the liquid resin produced. A pigment consisting of titanium dioxide and clay is incorporated.

ACID EMULSION PAINT. American Chemical Paint Co. Brit. Pat. 597,040, Applied for Feb. 16, 1945 (applied for in U. S. June 28, 1944); accepted Jan. 16, 1948. In the preparation of an acid emulsion paint in which an oily, film-forming part is dispersed, as an internal phase, in a continuous, aqueous acid external phase, a water-in-oil type emulsion of the film-forming ingredients is prepared and this emulsion is reversed by the incorporation of a reverser consisting essentially of substantially all of the aqueous acid desired in the finished paint at the time that the paint is to be used, the aqueous acid reverser constituting not over 10% by volume of the finished paint.

COATING CEMENTITIOUS SURFACES WITH SELF-HARDENING RESINOUS COMPOSITIONS. F. G. Mottershaw and G. J. L. Griffin (assigned to Semtex, Ltd.). Brit. Pat. 597,083. Applied for: Aug. 11, 1945; accepted Jan. 16, 1948. Cementitious surfaces are coated by first applying an acid-reacting film (e.g. phenol-formaldehyde, urea-formaldehyde or polyvinyl alcohol containing oxalic acid or sulfuric acid), which reacts with the free alkali present in the surface to form water-insoluble compounds therewith, allowing the treated surface to dry and then applying to the dry treated surface a self-hardening acidic resinous coating composition. The acid catalyst used in hardening the final coating is thus not uselessly neutralized by the alkali in the cementitious surface.

MARINE ANTI-FOULING PAINT. H. E. Smith. Brit. Pat. 597,657. Applied for: June 14, 1945; accepted Jan. 30, 1948. An anti-fouling, protective coating for ships' hulls, pontoons etc. made of metals, is produced by incorporating in a paint, varnish or lacquer at least 10% by weight of a phenyl mercury compound such as the borate, salicylate or phthalate. The use of at least 10% of the toxic agent is said to provide adequate protection against fouling by marine organisms and to lead to insignificant amounts of electrolytic corrosion.

SYNTHETIC RESIN COMPOSITIONS FOR USE AS CEMENTS AND COATINGS. W. Blackman and J. E. S. Whitney. Brit. Pat. 600,763. Applied for; Apr. 18, 1945; accepted Apr. 19, 1948. A base for a coating or adhesive composition is prepared by heating together rubber, a drying oil containing a conjugated double bond (tung oil and some varieties of dehydrated castor oil) and an acid-catalyzed phenol-aldehyde resin prepared from a para-alkyphenol (e.g. p-tertiary-amylphenol or p-tertiary-butylphenol) in the approximate proportions of 3:4:4 respectively, the duration and degree of heating being such that the drying oil must neither be pre-oxidized nor pre-polymerized beyond the point at which it is compatible with rubber.

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RECENT ADVANCES IN PAINT TECHNOLOGY

THE PROTECTION AND MAINTENANCE OF PETROLEUM PROPERTY. This report on the protection of maintenance of petroleum property points out that this practice is dependent largely on proper application and selection of protective coatings. In discussing the principles of good application practices, the author lists four fundamental requirements of protective coating maintenance: 1) surface preparation; 2) proper conditions for coating application; 3) adequate film thickness, and 4) material selection. Suggestions for the selection of materials are discussed in detail. One of the recommendations is the controlled and coordinated field testing under engineering guidance. C. R. F. Merkle. Petroleum Refiner **27**, 269-72 (1948).

OPTICAL LENS COATINGS. Twenty-nine coatings, spun on glass, have been given various mar and abrasion tests to determine if any one method can be considered reliable for comparing "soft" and "hard" plastics. It is concluded that the physical properties of the many plastics are so greatly different that no one test procedure can be considered satisfactory. Test methods employing such soft abrasive materials as cotton and cheese-cloth give erratic results because of polishing action, particularly noticeable with soft plastics. A given group of coatings will not necessarily rank in the same order for different mar and abrasion tests. Allymer CR-39 coating was the most resistant of all coatings to marring. It has the disadvantage of requiring curing in an inert atmosphere. An alkyd-modified melamine is considered second best and requires no inert atmosphere. Vibrin-1305, diallyl phthalate, and a combination of CR-39 (Dd) and diallyl phthalate, were also quite resistant. Silicone-2103, 3,3,5-trimethyl-cyclohexyl methacrylate, and Kotol coatings proved to be the most resistant to roof exposure and water immersion. End use should be stated before recommendations can be made for optical coating applications. H. W. Coles, W. F. Schulz, S. Levy and T. A. Wheatley. Modern Plastics **25**, 123-6, 167-70, 172, 174, 176-81 (1948), No. 11, July.

COMPARATIVE DETERMINATIONS OF THE DRYING TIME OF WHITE LEAD, TITANIUM WHITE, AND LEAD TITANATE STAND-OIL PAINTS WITH DIFFERENT DRIERS. To find out if titanium white and lead titanate paints need an addition of tung oil to the linseed oil to acquire the same drying time as white lead, 3 samples each of the above 3 paint types were tested in 3 series with amounts of driers ranging from 0.045 to 1.0 lead, 0.03-0.1 cobalt, 0.005-0.02% manganese, calculated on the vehicle and applied as naphthenates. The results show that with proper driers linseed-oil titanium white and lead titanate paints without tung oil dry just as fast as white lead paints and stand up well after aging. R. Dooper and B. J. Scheffer. Verfkroniek **21**, 38-9 (1948) (abstr. through Chem. Abs. **42**, 4367 (1948)).

ELECTRICAL PROPERTIES OF PAINT FILMS ON METALS. An investigation of the protective properties of paint films on metals immersed in sea water was made by measuring the electrical characteristics of such films and their changes with time. The electrode potential of painted mild steel plates immersed in an artificial sea water, and the apparent ohmic resistance and the apparent capacity of the paint film were determined, and the correlation of the electrical properties (potential, resistance and capacity) with the gradual spread of rusting was plotted. It is believed that the conception of the paint film as a "leaking condenser" provides a general explanation of the phenomena observed. It is suggested that the technique should prove valuable as a sensitive means of quantitatively following the breakdown of paint films on metals exposed to aqueous solutions. The method has possible alternative applications to the study of other types of protective coatings and thin films produced by corrosion inhibitors. F. Wormwell and D. M. Brasher. Nature **159**, 678-9 (1947).

CELLULOSE DERIVATIVES AS SUBSTITUTES FOR OIL-BASE COATINGS. In this article the author shows that the cellulose lacquers have little potentialities as substitutes for oil paints and varnishes. Oil base and cellulose derivative coatings have each found their own specific spheres of utility, and being radically different in constitution and characteristics, there is little room for one to encroach upon the other without serious loss of important properties. N. L. A. Pollard. Paint Manuf. **17**, 214-215 (1947).

CEMENT COATINGS. Information is given on the development and production, color range, mixing and application of cement coatings. These coatings if correctly mixed and used only on appropriate surfaces provide a decorative, hard, washable, protective coating under external or internal conditions. In view of the specialized character of their field of utilization, these coatings are thought to be unlikely to play any important part in oil conservation. Domestic, industrial and agricultural users are turning increasingly to them as a finish for buildings and an extensive market in foreign countries may be found where bright, light-reflecting exteriors affording insulation against the heat of the sun are required. Anon. Paint Manuf. **17**, 217-218 (1947).

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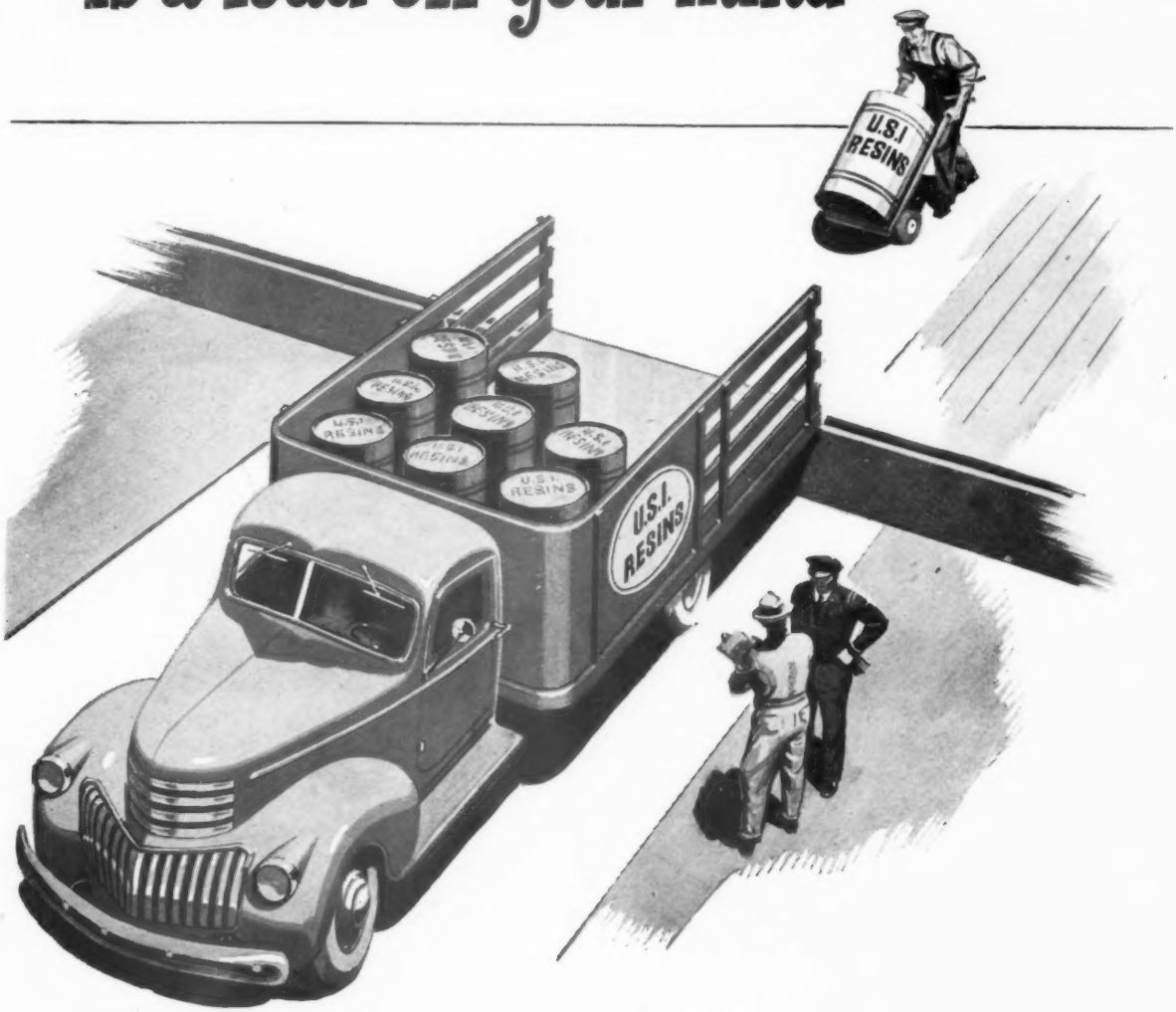

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